Admittance Spectroscopy of Deep Levels in CdTe Solar Cells

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ABSTRACT

Results of characterizing stressed and unstressed CdTe solar cells using admittance spectroscopy are presented herein. Measurements were performed in the frequency range from 20Hz to 30MHz and in the temperature range from 10°C to 100°C. Trapping states with a wide variety of characteristic frequencies were shown to exist in all cells studied. Estimates made using two separate methods show the trap concentration to be comparable to, or higher than, the bulk carrier concentration. The frequency and temperature dependence of both capacitance C(f, T) and conductance G(f, T) were used to provide estimates of the density of states function D_t, the capture cross section σ_t, and the position in the band gap E_t, for at least one trapping level/narrow band.

1. Introduction

A better understanding of trapping states and their influence on degradation is important for further improving the performance of CdTe thin film polycrystalline solar cells. Admittance spectroscopy (AS) electrical measurements, developed by Losee [1] and expanded upon by Cohen and Lang [2], have the potential to be an informative tool for characterizing trapping levels/bands in CdTe [3] solar cells.

2. Basics of the method

Due to band bending in the depletion layer of a cell, the Fermi level E_F crosses the trap level E_t at some distance from the interface, x_t (crossing point). The oscillating (testing) voltage causes the electric charge accumulated by traps to oscillate in the vicinity of x_t. Oscillating current due to trap recharging has both in-phase and out-of-phase components, providing the trap-related capacitance C_t and conductance G_t. These are connected in parallel with the common (unrelated to traps) diode capacitance C_d and conductance G_d (for a similar model used with CIS see ref 4). The trapped electric charge follows the applied voltage oscillations only if their frequency does not exceed the trap characteristic frequency, ω_t, which is mainly determined by the emission rate. Thus the total measured capacitance C_{tot} and conductance G_{tot} are described by the equations:

$$C_{tot} = C_d + C_t^o/[1+(\tau\omega)^2];$$
$$G_{tot} = G_d + G_t^o\{(\tau\omega)^2/[1+(\tau\omega)^2]\} \qquad (1)$$

where $\tau = \omega_t^{-1} = C_t^o/G_t^o$ is the trap characteristic time and ω is the angular testing frequency.

It is seen from Eqs. 1 that in the presence of traps, C_{tot} decreases and G_{tot} increases with increasing frequency. Comparison of measurements at high and low ω ($\omega_{HF} >> \omega_t$; $\omega_{LF} << \omega_t$) provides estimates of C_d, G_d, C_t^o and G_t^o:

$$C_d = C(\omega_{HF});\ G_d = G(\omega_{LF});\ C_t^o = C(\omega_{LF}) - C(\omega_{HF});$$
$$G_t^o = G(\omega_{HF}) - G(\omega_{LF}). \qquad (2)$$

In turn, comparison of C_t^o, G_t^o with C_d, G_d can be used to estimate the single-level trap concentration. In the case of several types of traps with different characteristic frequencies, this method could be used for the comprehensive estimation of the total trap concentration. To detect and study a particular trap state, an additional useful opportunity is provided by the analysis of the derivatives $dC/d\omega$ and $dG/d\omega$. Both derivatives should demonstrate peaks at the same frequency, ω_p, where $\omega_p=\omega_t/3^{1/2}$, and the magnitudes of these peaks are:

$$dC/d\omega|_{\omega p} = -[3\ (3)^{1/2}/8](C_t^o/\omega_t)$$
$$dG/d\omega|_{\omega p} = -[3\ (3)^{1/2}/8](G_t^o/\omega_t) \qquad (3)$$

The temperature dependence of a peak's (characteristic) frequency can be used to estimate the trap level position, E_t-E_v, and the capture cross section, σ_t. Assuming that the cross section is independent of temperature, the temperature dependence of ω_t is then determined by the equation:

$$\omega_t(T) = 2\sigma_t\, v_{Th} N_v \exp[-(E_t-E_v)/kT] \qquad (4)$$

Here v_{Th} is the average thermal velocity of holes, N_v is the effective density of states in the valence band. In CdTe at room temperature, $v_{Th} \cong 10^7$cm/s and $N_v \cong 1.5\times10^{19}$cm^{-3}. The E_t-E_v value and the capture cross section are determined respectively from the slope of the graph $\ln[\omega_t T^{-2}]$ vs 1/T and from its intersection with the axis 1/T=0.

3. Experimental results and discussion

The cells studied were fabricated at First Solar, LLC. (FS) with CdS and CdTe deposited using vapor transport on SnO_2:F-coated soda-lime glass substrates. In order to study potential degradation mechanisms, back contact processes and stress conditions were selected to provide significant degradation (~ 25% loss in efficiency and 15% loss in V_{oc}). The admittance spectra were measured using LCR meters in the angular frequency range of $\omega \cong 126$ to 1.8×10^8 s^{-1}. The oscillating voltage amplitude was 0.01 V. The $C(\omega)$ and $G(\omega)$ spectra measured on as-prepared and stressed cells had the same major features. A decrease in capacitance of more than two times and an increase in conductance by two orders of magnitude in the range $\omega<6\times10^5$Hz exist. This indicates a total trap concentration exceeding the "doping level" found from C-V measurements to be ~5×10^{14}cm^{-3}.

For studying slow (deep) traps, the transients in capacitance and conductance were measured via a switching applied bias: 0V → –1V→ 0V, while holding at –1V for about two minutes. The testing voltage frequency was 1MHz. Even 5 or more minutes after switching back to V_{bias} = 0, the C value did not return to its initial value. It is unclear whether the observed long-term relaxation is totally due to the recharging of slow electronic states, or if there is some contribution of migration and spatial redistribution of highly mobile ions such as Cu_i^+. If the difference in the C values before and immediately after exposure to the reverse bias is due to slow traps (τ >3sec), then the concentration of these very slow traps should be greater than 2N.

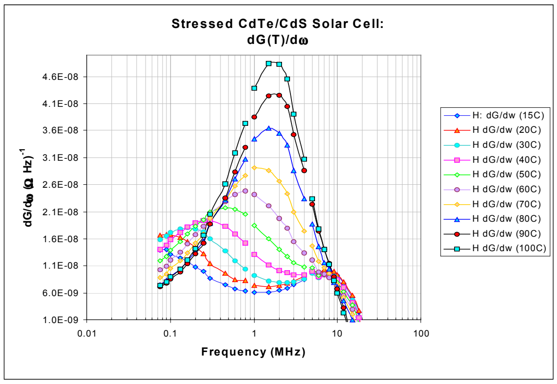

Fig.1. dG(T)/dω vs frequency for a stressed CdTe/CdS cell.

The analysis of the capacitance and conductance derivatives upon frequency revealed peaks that could be attributed to a single level or narrow band of traps. The peak frequencies differ for the as-prepared and stressed cells. For the former, $\omega_{t1} \cong 6x10^6 s^{-1}$ at room temperature, while for the latter, $\omega_{t2} \cong 6x10^5 s^{-1}$. Another difference is that the stressed cells demonstrate a considerable shift of characteristic frequency ω_{t2} with increasing temperature (see Fig. 1), while ω_{t1} shifts only slightly. The latter contradicts simple theory and demands more thorough studies of its nature and the corresponding electronic states in the as-prepared cells. Using the data presented in Fig. 1 for the stressed cell, the energy of the trap level and the capture cross section were determined as described in Sec.2. The obtained value E_t-E_v=0.37eV agrees with the level for Cu_{Cd} substitutionals [5,6]. The capture cross section $\sigma_t \cong 1x10^{-15} cm^2$ does not seem unreasonable for a singly charged trap for holes.

To obtain additional information on the trap density of states (DOS) function, $D_t(E_t)$, we have used the method developed in [7]. The $D_t(E_t)$ is derived from the C(ω) spectra using the equations:

$$D_t(E_t) = -FU_d/(qx_d)(dC/d\omega)(\omega/kT);$$
$$E_t = kT \ln[2v_{Th}(T)\sigma_t N_v(T)/\omega]; \quad F = [U_d/q(E_t-E_F)]^{1/2}, \qquad (5)$$

where U_d is the band bending over the depletion layer. In our calculations we used E_t=0.37eV as determined above, and the Fermi level E_F was calculated based on the carrier concentration value derived from the C-V profile. The $D_t(E_t)$ function obtained in this way for the stressed cell is presented in Fig. 2. The major features are as follows: (1) the trap level is considerably broadened, the trap band width at half of the maximum $D_t(E_t)$ value is about 0.05eV; (2) integrating the DOS function over E_t provides the trap concentration $N_t \cong 1x10^{15} cm^{-3}$, which is close to the doping level N. The expression for the F factor (see Eqs.5) is valid only if the trap concentration is much less than the doping level. Our preliminary analysis based on refining the theory presented in [7] shows that the maximum DOS value should be increased and the shape of the DOS peak corrected.

To clarify the influence of processing procedure, AS measurements were performed on cells with FS CdS/CdTe material with the ZnTe:Cu/Au and Cu/Au back contacts completed at CSM. The major features of the capacitance and conductance spectra were in general similar to those for the FS cells. In particular, the total trap density was found to exceed the doping level. At least two well pronounced peaks in dG/dω were found for each cell; one in the frequency range of 0.1 to 1 MHz, and the other at about 10 KHz. The positions and magnitudes of these peaks varied for cells with different back contacts and changed after stressing.

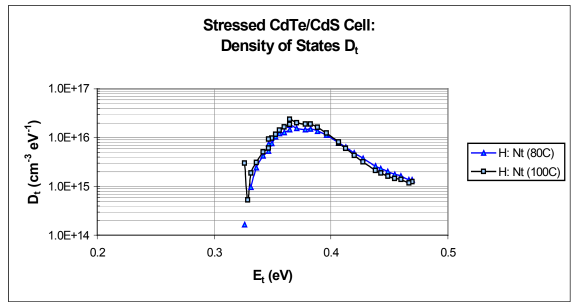

Fig. 2. Density of states for a stressed CdTe/CdS cell.

4. Conclusions

The results obtained show that admittance spectroscopy can be successfully used for detecting and studying traps in CdTe solar cells and to monitor the influence of processing procedures and stressing. It was found that the total concentration of different types of traps could considerably exceed the doping level in CdTe. The characteristic times of traps, hence their energy level positions, vary widely. There exist high concentrations of very slow (deep) traps that can be presumably attributed to grain boundary states. Trap bands with energies around 0.35eV above the valence band may be attributed to the Cu_{Cd} substitutions. The energy level of these traps is broadened to a band with a width of about 0.05eV.

5. Acknowledgements

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